

Hopping Conductivity in Polycrystalline Diamond Films

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Abstract—The results of the experimental study of the conductivity of a polycrystalline diamond film by dielectric spectroscopy are presented. A diamond film about 200 μm thick was grown by microwave plasma-assisted chemical vapor deposition for 180 h. Two pronounced local peaks in the frequency dependence of the conductivity were observed. The relevant frequencies were temperature-dependent. These data permit us to hypothesize that the hopping mechanism of conductivity occurs in the polycrystalline diamond film. Two types of electrically active centers with different activation energies and relaxation times are involved in the conductivity.

Key words: polycrystalline diamond, chemical vapor deposition, dielectric spectroscopy.

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1. INTRODUCTION

Diamond is an attractive material for high-frequency and high-temperature electronics due to its unique chemical, thermo- and electro-physical, mechanical and other properties [1]. However, the usage of natural or synthetic diamond single crystals and epitaxial diamond films is restricted due to their high cost. In some cases polycrystalline diamond films (PCDFs) may be used in electronic devices. In contrast to single crystals and epitaxial films, PCDFs may be obtained by relatively simple and developed methods of chemical vapor deposition (see, e.g., [2, 3]). The properties of PCDFs may change considerably depending on the characteristics of their polycrystalline structure. This necessitates investigations aimed at clarifying the features of the physical properties of PCDFs and the relevant mechanisms. The study of PCDFs is of particular interest because it is possible to produce these films with a large area having highly homogeneous electrical properties [1].

Dielectric spectroscopy is one of the most informative methods used to study the conductivity of materials. A number of papers present the results of studying diamond films by this method (see, e.g., [4–7] and references therein). As a rule, the PCDF material is considered in such investigations as being electrically homogeneous [7]; however, in a series of papers it is noted that the heterogeneity of the film structure plays an important role. This heterogeneity is due to the fact that during the formation of a diamond film regions composed of disordered graphite-like material are formed between the diamond crystallites composing the film. The higher conductivity of the inter-grain boundary material results in the formation of the high density of the electrically active defects. In the films

produced by the gas-phase deposition the crystallites are elongated along the growth direction (i.e., perpendicular to the substrate surface). This permits the formation of the percolation current-conducting paths on the grain boundaries. On the basis of the mentioned properties of the grain boundaries, in a series of papers it is concluded that the conductivity of PCDFs is mainly determined by the grain boundaries (see, e.g., [8]). It should be noted that in some papers the mechanism of the PCDF conductivity is considered as a superposition of the charge transfer along the grain boundaries and charge transfer directly via the diamond crystallites. Each process dominates in a certain temperature and frequency range [9–11]. Most researchers agree that the main mechanism of the charge transfer in both film components is hopping conductivity [4–13]. This conclusion is obvious in the case of grain boundaries, because hopping conductivity is the main mechanism of conductivity in systems with low ordering. In the case of diamond crystallites, hopping conductivity is possible due to the defects in the crystal structure and the relevant additional electron energy levels.

The most important parameters determining the mechanism of hopping conductivity are the activation energy of the corresponding levels and the frequency dependence of conductivity. To obtain information about these parameters the frequency and temperature dependences of the PCDF complex dielectric permeability were studied in this paper.

2. EXPERIMENTAL

PCDF complex dielectric permeability was studied on an impedance analyzer made by Novocontrol Tech-

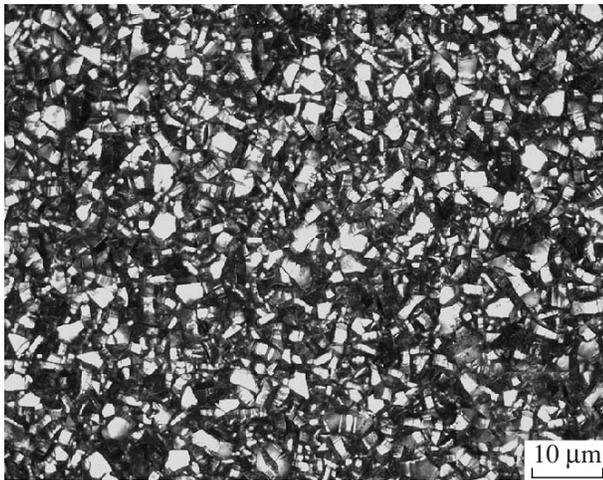


Fig. 1. Microscopic image of the top PCDF surface.

nologies. A PCDF sample was fixed between two gold electrodes, with their area being smaller than that of the sample. Alternating voltage with an amplitude of 1 V was applied to the electrodes. The voltage frequency was changed from 10^{-1} to 10^7 Hz. These measurements were carried out in the temperature range of 273–423 K. The temperature was controlled by supplying nitrogen of the necessary temperature into the measuring capsule. The nitrogen supply ensured an inert atmosphere as well.

The value of the current passing through the capacitor formed by electrodes provides information about the conductivity of a substance between its plates. The phase shift of the current with respect to the voltage allows one to determine the real part of its complex dielectric permeability. The imaginary part of the complex permeability is determined by the electroconductivity of the substance (σ) and frequency (ω): $\varepsilon''(\omega) = i \frac{4\pi}{\omega} \sigma(\omega)$ [14]. The analysis of the frequency dependences of the real and imaginary parts of the dielectric permeability provides information about the characteristic times of the charge transfer in the substance and the charge carrier type.

A PCDF was used as a sample in the investigations. The film was grown on a silicon substrate by using the microwave discharge activation of the hydrogen-methane gas mixture. The methane concentration in the gas mixture was about 1% and the substrate temperature during deposition was kept at the level of 850°C. The continuous deposition lasted for 180 hours, resulting in a film 200 μm thick.

After deposition of the diamond film the silicon substrate was etched in a mixture of hydrofluoric and nitric acids. The bottom part of the free film is smooth and repeats the structure of the polished substrate surface. The top film surface is formed by the facets of the dia-

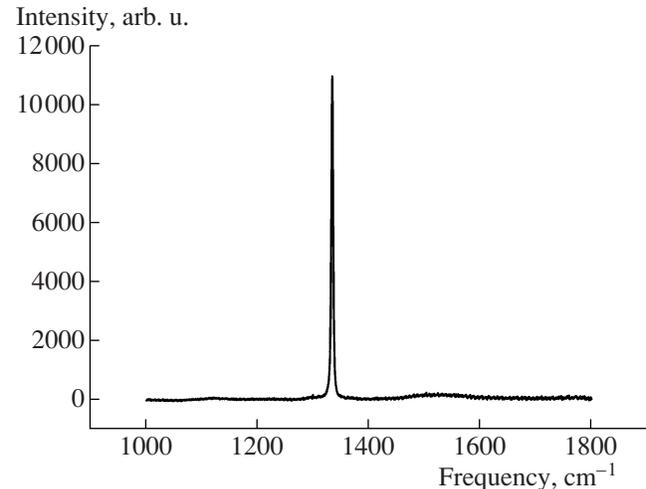


Fig. 2. Raman spectrum of the PCDF. The excitation wavelength $\lambda = 514.5$ nm

mond crystallites forming the film. As a result, it has the roughness of about 5 μm . The largest crystallites are of an irregular pyramidal form typical for the directional growth of the polycrystalline films. The bases of crystallites forming the upper film surface have the linear dimensions of about 5 μm . The typical optical microscopy image of the film surface is given in Fig. 1.

To determine its phase composition, the film was analyzed by Raman spectroscopy. The Raman spectra were identical for both sides of the film due to its high transparency. Figure 2 shows the Raman spectrum with an intense narrow line at the frequency of 1330 cm^{-1} corresponding to a high quality diamond crystal. A broad line in the region of 1580 cm^{-1} demonstrates the presence of a small amount of nondiamond (i.e., graphite-like) carbon.

To carry out measurements on an impedance analyzer a film sample of about 1 cm^2 was washed in an ultrasound basin with isopropyl alcohol. Both sides of the film were covered with silver paste.

3. RESULTS AND DISCUSSION

The impedance analyzer used in this paper allowed one to measure the imaginary part of the dielectric permeability. Figure 3 shows the diagram with the results of measurements carried out at various temperatures and frequencies. At each temperature the frequency dependence of the imaginary part of the dielectric permeability was approximated by the sum of two Havrilyak-Negami terms (see, e.g., [15]) taking into account the conductivity at the constant voltage. Two maxima are the characteristic feature of the frequency dependences $\varepsilon''(\omega)$. These dependences may demonstrate the presence of two conductivity mechanisms in the material: low-frequency (10^1 – 10^2 Hz) and high-frequency

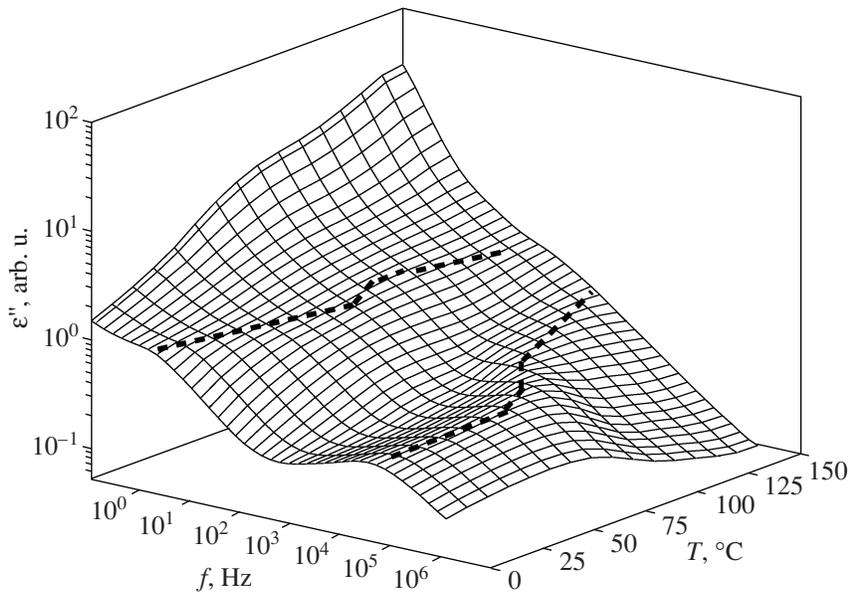


Fig. 3. Three-dimensional frequency and temperature dependences of the imaginary part of the dielectric permeability. Dotted lines show the shift of the frequency dependence peaks as the temperature is changed.

(10^4 – 10^5 Hz). The positions of these maxima correspond to the characteristic times of the charge transfer.

The peak positions in the $\epsilon''(\omega)$ dependence are temperature-dependent showing that the charge transfer is temperature-activated. These processes are conveniently analyzed with the Arrhenius diagram for the frequency corresponding to the maximum. If the process

follows the Arrhenius law $\left(\omega_{\max} \sim \exp\left(\frac{E_a}{kT}\right)\right)$, then the

experimental points should fit the line with a negative slope, with its modulus being the activation energy of the process. Figure 4 shows the Arrhenius diagrams for both maxima in the frequency dependences. It is seen that in both cases the charge transfer follows the Arrhenius law at temperatures up to 320 K. In this region the activation energies are 0.063 eV for the high-frequency and 0.18 eV for the low-frequency conductivity. At other temperatures a unexpected decrease of the frequencies of the maxima in the $\epsilon''(\omega)$ as the temperature is increased is observed.

To determine the possible reasons for this behavior the change of the PCDF conductivity with frequency and temperature was analyzed. The results of this analysis are presented in a diagram shown in Fig. 5. The general form of the isothermal sections of the $\sigma(\omega, T)$ surface is described by a linear function with a slope of about 0.8. The $\sigma \sim \omega^{0.8}$ dependence demonstrates hopping conductivity [14]. The analysis of the curves obtained at different temperatures allows one to assume a nonrandom character for the shifts from the linear dependence and to conclude that the dominating conductivity mechanism changes in the frequency range of 10^2 – 10^4 Hz.

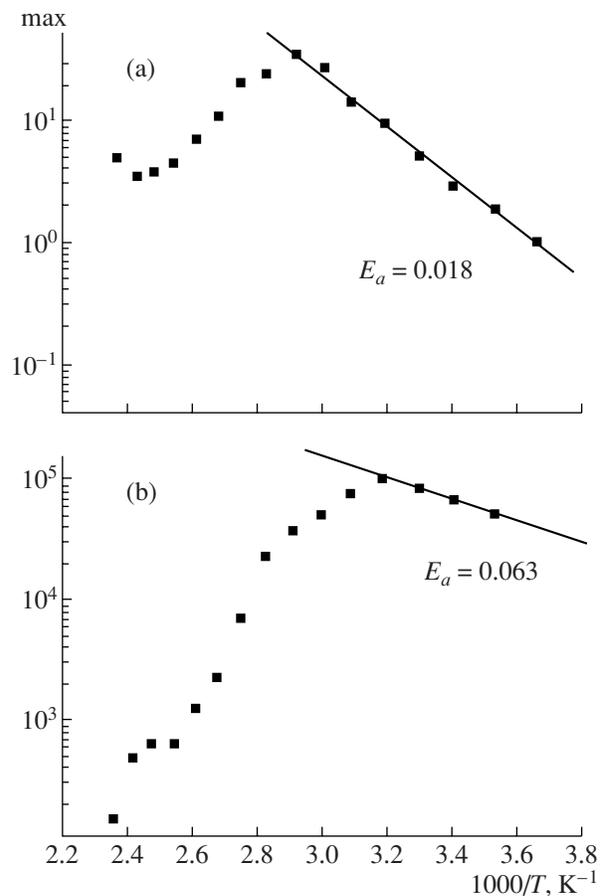


Fig. 4. Arrhenius diagram of the temperature dependence of the maximal absorption frequency for each conductivity mechanism. a, low-frequency conductivity; b, high-frequency conductivity.

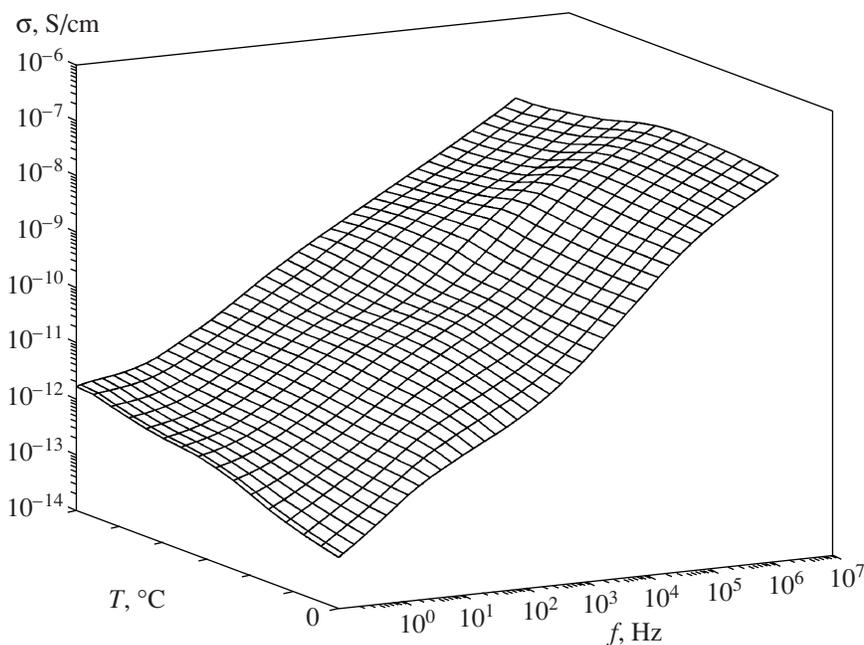


Fig. 5. Three-dimensional diagram of the frequency and temperature dependences of conductivity.

The above data allow one to conclude that at low frequencies the conductivity mechanism is hopping conductivity along the grain boundaries. A number of researchers emphasize that the activation energy of this process is 0.3 ± 0.1 eV (see, e.g., [16]) corresponding well with our data within the experimental accuracy.

The high-frequency conductivity mechanism may be also explained by the hopping transfer of charge carriers. The values of conductivity and dielectric permeability at the activation of this mechanism and the characteristic relaxation times demonstrate that this process takes place inside diamond crystallites [17]. The activation energy of this process corresponds to the narrow levels formed in the energy structure of crystallites with the introduction of nitrogen atoms into the diamond lattice [17]. The above conductivity mechanisms are characteristic of PCDFs up to 10^2 μm thick [16].

It should be noted that on the $\sigma(f, T)$ surface there is an inflection in the high-frequency region at about 320 K, coinciding with the point of the change in the trend of curves on the Arrhenius diagram. In [18] anomalies in the conductivity curves at temperatures close to room temperature are attributed to the influence of the contact zone.

4. CONCLUSIONS

The impedance of the PCDF sample was measured at temperatures of 273–423 K and frequencies of 10^{-1} – 10^7 Hz. Two conductivity mechanisms with the characteristic relaxation times of 10^{-1} and 10^{-4} s were revealed. On the basis of the analysis of experimental data it was concluded that both conductivity mecha-

nisms are of the hopping type. Grain boundaries are responsible for the low relaxation times and diamond crystallites for the high relaxation times. Hopping conductivity is caused by the disordering of the carbon material in the region of grain boundaries and energy levels formed by the introduced nitrogen atoms in the region of crystallites.

These results demonstrate that mechanically stable PCDFs up to 200 μm thick and with properties analogous to those of PCDFs that are less thick can be grown.

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